

# The semiconductor-to-ferromagnetic-metal transition in FeSb<sub>2</sub>

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## Abstract

We propose FeSb<sub>2</sub> to be a nearly ferromagnetic small gap semiconductor, hence a direct analog of FeSi. We find that despite different compositions and crystal structures, in the local density approximation with on-site Coulomb repulsion correction (LDA+ $U$ ) method magnetic and semi-conducting solutions for  $U=2.6$  eV are energetically degenerate similar to the case of FeSi. For both FeSb<sub>2</sub> and FeSi (FeSi<sub>1-x</sub>Ge<sub>x</sub> alloys) the underlying transition mechanism allows one to switch from a small gap semiconductor to a ferromagnetic metal with magnetic moment  $\approx 1\mu_B$  per Fe ion with external magnetic field.

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The unusual crossover from a small gap semiconductor at low temperatures to a metallic state with enhanced magnetic fluctuations above room temperature observed in FeSi has long been a subject of great interest<sup>1,2,3,4,5</sup>. Two different models have been proposed to explain this anomaly. One proposal is that FeSi is a Kondo insulator<sup>2</sup>. The second is that FeSi is a nearly ferromagnetic semiconductor<sup>3,4</sup>. This latter proposal is supported by *ab initio* electronic structure calculations using the LDA+*U* method<sup>6</sup> which found that a ferromagnetic metallic state was very close by in energy<sup>3</sup>. Further support for this second model comes from the direct observation of this semiconductor-metal transition as the lattice is expanded by the isoelectronic substitution of Ge for Si<sup>7</sup>. In order to determine critical magnetic field a minimal two-band model with interband interaction was suggested. Even in the mean field approximation the model nicely describes the full phase diagram of the FeSi<sub>x</sub>Ge<sub>1-x</sub> alloy series<sup>7</sup>.

Recently, a second Fe-compound, FeSb<sub>2</sub>, was found to have a similar crossover as FeSi from a small gap semiconductor to a metallic state with strong magnetic fluctuations<sup>8,9</sup>. This raises immediately the question whether *ab initio* calculations confirm the close analogy between the two Fe compounds. This is a nontrivial question since these electronic structure calculations show strong hybridization between the Fe-3*d* orbitals and the *s-p* electrons of the close Si or Sb neighbors. This strong hybridization clashes with the assumption of weak hybridization between localized and itinerant electrons that underlies a Kondo insulator description and makes it difficult to relate the Kondo insulator model to the *ab initio* electronic structure. However in view of the differing compositions and crystal structures of FeSi and FeSb<sub>2</sub> it is by no means obvious that closely similar models can be derived from *ab initio* electronic structure calculations for both compounds. For this reason it is clearly important to examine FeSb<sub>2</sub> closely.

FeSb<sub>2</sub> crystallizes in the marcasite crystal structure<sup>10</sup>. Each Fe atom is surrounded by a slightly distorted octahedron of Sb neighbors with 2 neighbors at 2.57 Å and 4 at 2.59 Å. The octahedra are corner sharing in the *ab* plane and edge sharing along the *c*-axis.

The results of density functional calculations using a local density approximation (LDA)<sup>11</sup> within TB-LMTO-ASA program<sup>12</sup> are shown in Figures 1 and 2 (the calculations were performed without spin-polarization). Atomic spheres radii were chosen as R(Fe) = 2.67 a.u. and R(Sb) = 2.99 a.u., in ASA approximation to fulfil the volume 6 classes of empty spheres were inserted with radii from 1.56 to 0.81 a.u. The overall bandwidth is  $\approx 10$  eV

with strong Fe-Sb hybridization due to the short Fe-Sb bonds. The density of states (DOS) is shown in Figure 1. The Fermi energy lies in a small band gap similar to the case of FeSi. Also in Figure 1 the DOS broken down in Fe- $3d(t_{2g})$  and Sb- $4p$  states is displayed. Narrow bands appear above and below the band gap with predominantly  $3d$  character – again similar to the case of FeSi. There is however a substantial contribution of the Sb- $4p$  states to valence band peak just below the Fermi energy but in the interval from the Fermi energy to  $\approx 1$  eV Sb- $4p$  states are presented very weakly.

The band structure of FeSb<sub>2</sub> is presented in Figure 2(a). There is a small indirect energy gap with the minimum in the conduction bands lying on the GZ-lines and the maxima of the valence band is at the R-point. The narrow peak in the DOS at the bottom of the conduction band arises from the flat bands that extend over roughly half of the Brillouin near the Z- and R-points. The orbital character of these flat bands is predominantly  $3z^2 - r^2$  (in the global coordinate system) as illustrated in Figure 2(b). These are  $3d$  orbitals pointing away from the Sb-sites in the octahedra surrounding the Fe atoms. The top of the valence band lies mostly in the DOS peak  $\approx 0.3$  eV below the conduction band and has predominantly  $3d$  ( $x^2 - y^2$ )-character. There is however a small density of states with mostly Sb- $p$  character which is responsible for the small indirect band gap.

The main feature of the LDA band structure is this small gap ( $\approx 0.3$  eV) between relatively flat bands of  $3d$  character giving rise to sharp peaks in the DOS. But the Sb- $4p$  band contributes small density of states in this gap with zero at the Fermi level. In reference<sup>13</sup> from measurements of optical reflectivity the semiconducting optical gap was estimated as  $E_g = 0.035$  eV. This value is larger than that obtained from the resistivity measurements  $\approx 0.02$ - $0.025$  eV (see reference<sup>9</sup>). This situation is similar to FeSi except that  $E_g$  does not show any dependence on temperature up to the crossover temperature.

The LDA approximation was extended to allow for spin and orbital polarization by Anisimov *et al.*<sup>6</sup> by introducing a local Coulomb repulsion,  $U$ . This LDA+ $U$  method when applied to FeSi found that there was a ferromagnetic metallic state very close by in energy to the small gap semiconducting state of the LDA. The exact energy difference between the two depends on the choice of  $U$ . This result of LDA+ $U$  is nicely confirmed by the fact that the isostructural-isoelectronic compound FeGe has the ferromagnetic metallic ground state. Actually if spin-orbit terms were included the ferromagnetism of FeGe would develop a long period spiral structure as observed in practice due to the presence of a Dzyaloshinskii-Moriya

term in resulting from the absence of inversion about the Fe sites.

The phase diagram of the  $\text{FeSi}_x\text{Ge}_{1-x}$  alloys can be reproduced by choosing the reasonable value of  $U$ , an onsite Coulomb repulsion on the Fe sites of  $U=3.7$  eV<sup>7</sup>.

We have applied the LDA+ $U$  method to  $\text{FeSb}_2$ . As in the case of  $\text{FeSi}$  a second local minimum appears in the energy vs. uniform magnetization at a value of  $1 \mu_B$  per Fe (see Figure 3). In this set of calculations we performed fixed spin moment procedure<sup>3</sup>. Again the exact energy difference between the two minima is dependent on the value of  $U$ .

In all our calculation we used the value  $J_H=0.88$  eV for the exchange (Hund's) Coulomb parameter but varied the value of direct Coulomb parameter  $U$ . As a result, in  $\text{FeSb}_2$  we found the critical value of the direct Coulomb parameter  $U_c=2.6$  eV. As in  $\text{FeSi}$  and  $\text{FeSi}_x\text{Ge}_{1-x}$  alloys, for any value of the  $U$  parameter less than  $U_c$  it is the nonmagnetic ground state that is lower in total energy. Otherwise for the  $U$  values above  $U_c$  ferromagnetic state is lower in energy. Only for  $U_c$  these two states have the same energy.

Comparison of the total  $\text{FeSb}_2$  density of states near the Fermi energy to  $\text{FeSi}$  is shown in Figure 4.

The close similarity between the LDA+ $U$  results for  $\text{FeSi}$  and  $\text{FeSb}_2$  agrees well with the close correspondence in their properties. It demonstrates the nearly ferromagnetic character of these small gap semiconductors.

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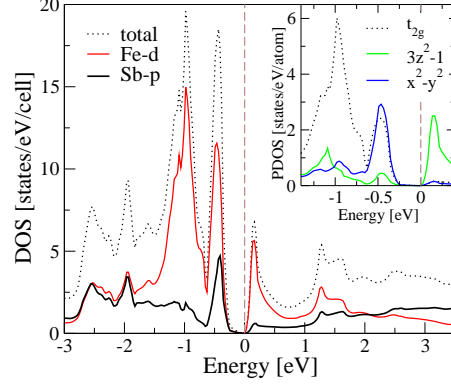


FIG. 1: Total and partial densities of states for  $\text{FeSb}_2$  from the LDA calculation. Inset shows partial  $t_{2g}$ -DOS and  $3z^2 - r^2$ ,  $x^2 - y^2$  orbitals DOS of Fe-3d states. The Fermi energy corresponds to zero.

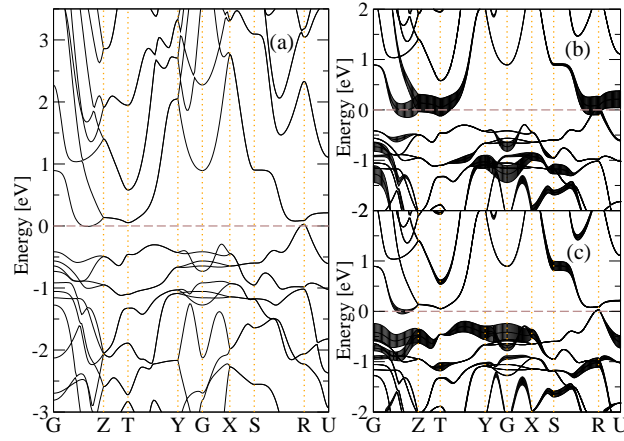


FIG. 2: (a) Band structure of  $\text{FeSb}_2$  from the LDA calculation. Right panels show partial contributions of (b)  $3z^2 - r^2$  and (c)  $x^2 - y^2$  orbitals to the total band structure. Additional broadening of the bands corresponds to the contribution of the orbital. The Fermi energy corresponds to zero.

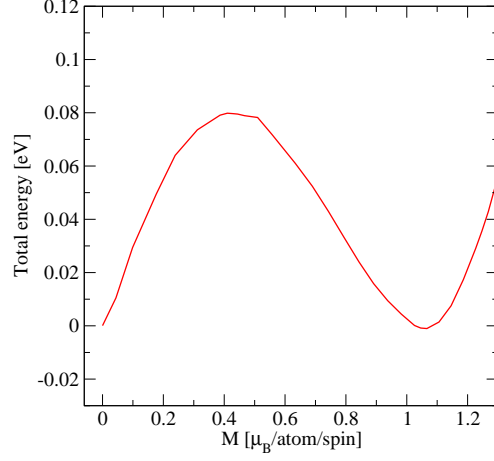


FIG. 3: Total energy dependence on magnetization value for FeSb<sub>2</sub>. From the LDA+ $U$  calculation with  $U=2.6$  eV and  $J_H=0.88$  eV. Energy is related to the energy of nonmagnetic state.

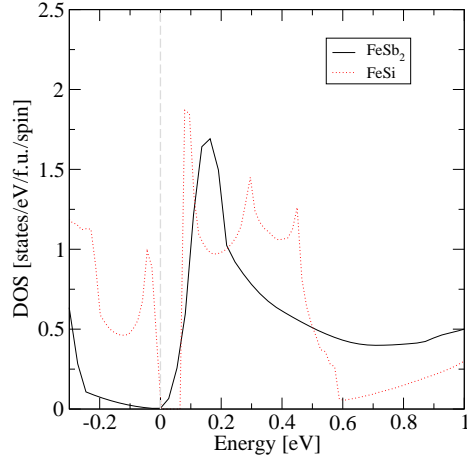


FIG. 4: Total densities of states of FeSb<sub>2</sub> and FeSi<sub>3</sub> from the LDA calculations near the Fermi energy.